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CONTENTS

APPLIED ELECTRON MICROSCOPY[1]

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Abstract

This paper is in two sections. The first includes: (i) a description of the technique of taking stereoscopic photographs with the electron microscope, (ii) an investigation of particle sizes in mine dust, and (iii) the use of electron diffraction technique in conjunction with an electron microscope. This last subject is illustrated by a study of clays and other paper-coating materials.

The second section includes several applications of the Toronto instrument to botanical investigations. Examples of the usefulness of the instrument in this field are: (i) a method of photographing the cuticle of *Antirrhinum majus* L. var. *Rosalie*, (ii) a study of the wall structure of *Aloe arborescens* Mill. subjected to different chemical treatments, and (iii) stereoscopic views of broken flax fibres.

I. STEREOSCOPIC PHOTOGRAPHY WITH THE ELECTRON MICROSCOPE

One of the most important advantages of the electron microscope, especially for biological research, is its large depth of focus (D.F.). This depth is much greater than the linear dimensions of the objects usually examined. By differentiation of the simple lens formula it can be shown that the depth of focus is given by:

$$\text{D.F.} = \frac{2f^2}{(v-f)^2} \cdot \frac{R}{a} \cdot \frac{v}{u},$$

where f = focal length in centimetres,

R = radius of the allowable spurious disk in the image plane,

$= \frac{v}{u} (0.005)$ microns,

v = image distance in centimetres,

u = object distance in centimetres,

a = aperture in radians.

With typical values of these constants, viz., $f = 0.5$ cm., $v = 50$ cm., $u = 0.5$ cm., $R = \frac{v}{u} (0.005)$ microns, and $a = 0.001$ radian, the D.F. = approximately 10 μ. In optical microscopes the highest resolution is obtainable using lenses with a numerical aperture of 1.25 or more, when the depth of focus shrinks to the order of 0.4 μ with visible, or 0.2 μ with ultraviolet, radiation.

Even with resolution much better than is assumed in the representative case for the electron microscope above, the depth of focus will still be comparatively greater (in proportion to the resolution) than can be obtained with an optical microscope.

The large depth of focus has made possible the adaptation of the instrument for stereoscopic photography. After a picture is taken, the object is tilted through a small angle and a second picture of the same field is taken in the second position. These two pictures are used in the ordinary manner to give a stereoscopic view of the specimen. Typical stereoscopic pairs of pictures are shown in Figs. 1 and 2. The first pair is a view of zinc orthosilicate crystals and the second pair gives a view of smoke particles clinging to a fibre of rubber. It is interesting to note in the second view the manner in which the particles build up one upon another.

A special object holder cartridge, designed by Hillier, is used to secure these photographs (Fig. 3). The cartridge is composed of two cylinders, with the axis of the small one at an angle of 6° to that of the large one. The axis of the large cylinder is parallel to that of the microscope when the picture is being taken. The object holder, which is a mesh of fine wire, is situated under a small metal cap at the end of the cartridge.

The working of the holder in taking stereoscopic views is illustrated in Fig. 4. Let it be assumed that a first photograph has been taken with the two cylinders (marked A and B) in the positions designated by the dots. After the first exposure of a chosen field has been taken, the holder is removed from the microscope and B is rotated through 180° to its intermediate position relative to A. The cartridge is then rotated through 180° as a unit until the cylinders occupy the final positions as shown in the third figure. The holder is returned to the microscope in this position and a second photograph is taken of the same field. By this procedure the object is tilted through 12° and the relative position of the object with respect to the beam is unaltered. Twelve degrees is the approximate angle subtended by the distance between normal human eyes at a distance of 25 cm. from the eyes. This method of tilting the object by two rotations is necessary because it is unsatisfactory, mechanically, to attempt to tilt the object directly, although such a direct tilting process would serve just as well if it could be done easily and accurately.

The hole in the lower end of the cylinder B has a diameter of 0.5 mm. and it leaves 12 openings in the mesh uncovered to the electron beam. The operator can easily examine the 12 openings and with the aid of a map of the field can rediscover the particular field to be photographed the second time.

In Figs. 5 and 6 are two further examples of the use of stereoscopic examination of specimens by the electron microscope. Fig. 5 is a stereoscopic view of a polishing powder of silicon dioxide, and Fig. 6 is a view of a much finer optical polishing powder.

PLATE I

ZINC ORTHOSILICATE

X 1500

FIG. 1

X 1200
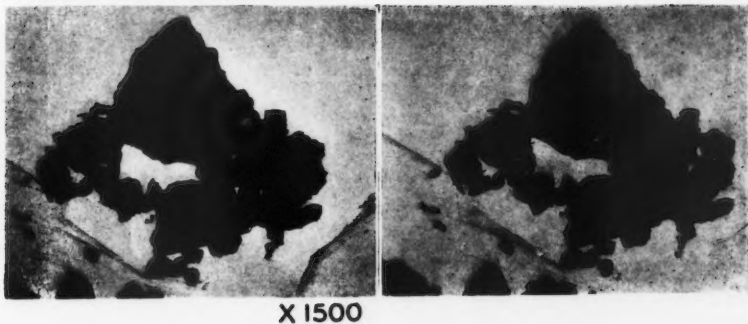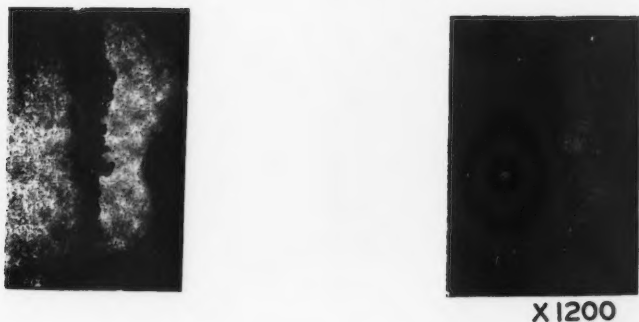
FIG. 2

FIG. 1. *Stereoscopic view of zinc orthosilicate crystals taken with the electron microscope at a magnification of ×1500.* FIG. 2. *Stereoscopic view of smoke particles caught on a rubber fibre and photographed with the electron microscope at a magnification of ×1200.*

PLATE II
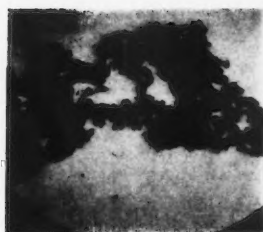
X 1200

FIG. 5
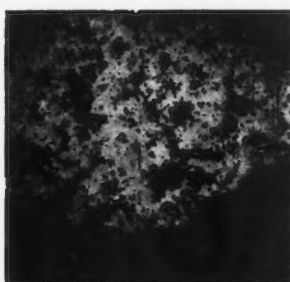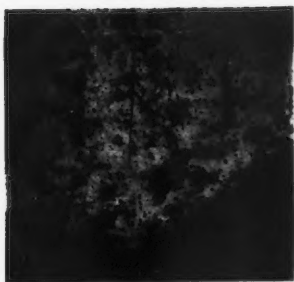
X900

FIG. 6

FIG. 5. *A stereoscopic view of a silicon dioxide polishing powder.* ×1200. FIG. 6. *A stereoscopic view of a much finer optical polishing powder.* ×900.
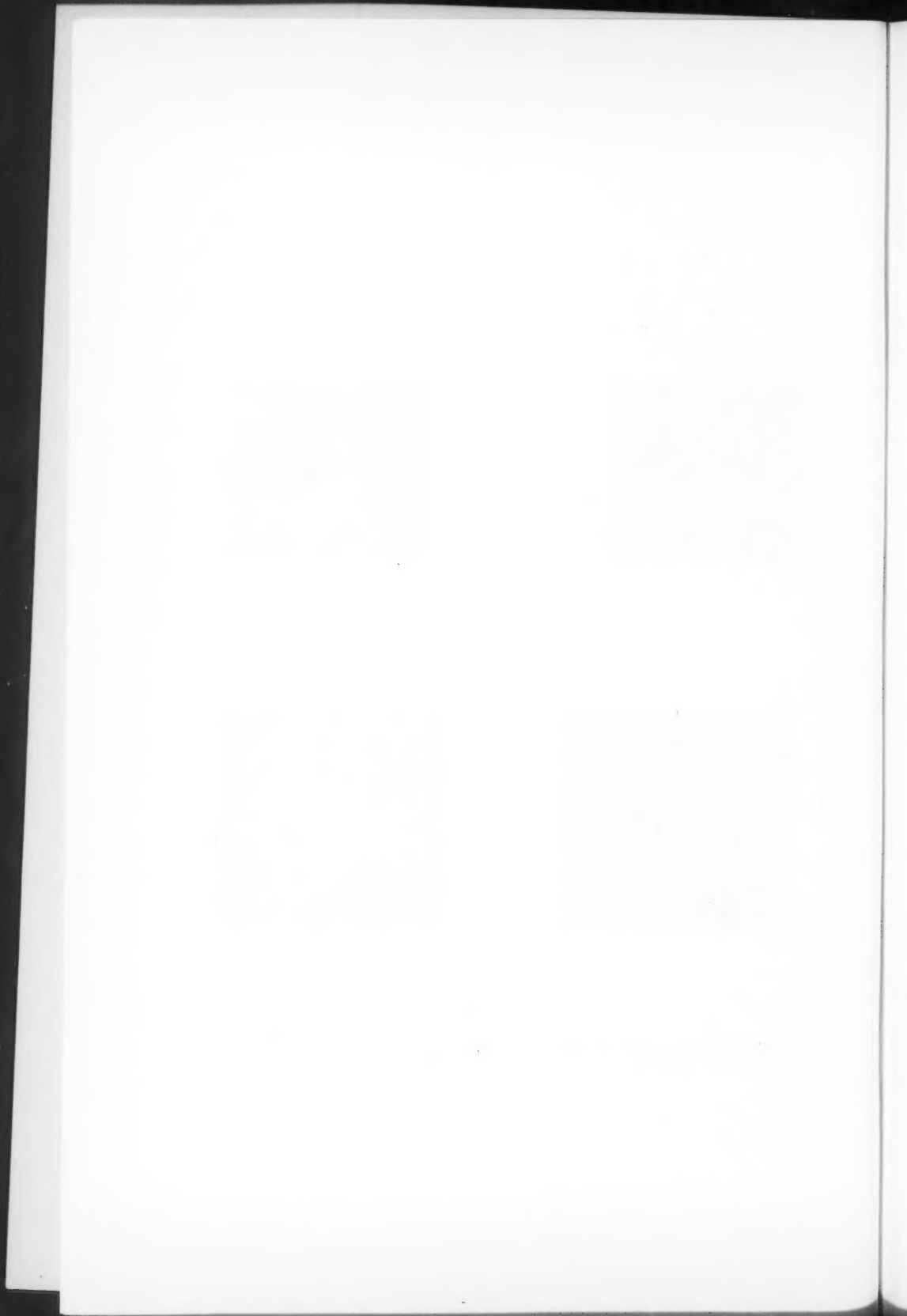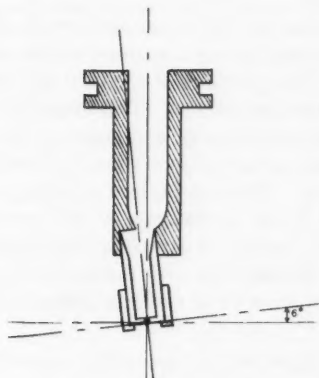
FIG. 3. *The special object holder used for securing stereoscopic photographs in the electron microscope.*
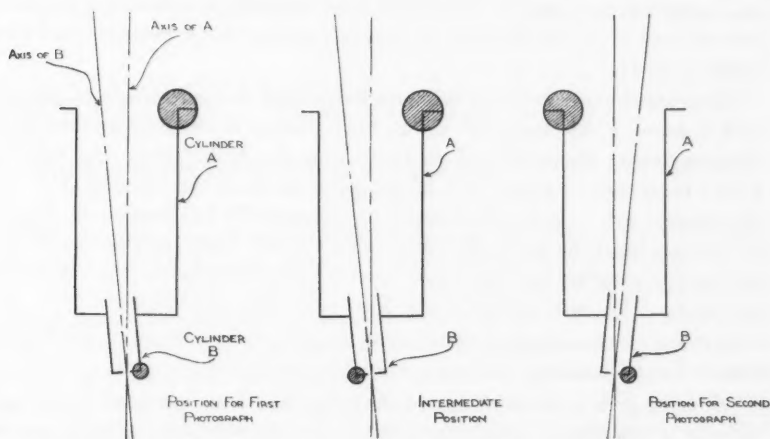
FIG. 4. *Schematic drawings used to explain the use of the special object holder when obtaining a stereoscopic view with the electron microscope.*

Particle Sizes in Mine Dust

Drilling and blasting operations produce silica dust in the air of a mine. If this dust is breathed into the lungs over long periods of time the condition known as silicosis, which is a serious disease among miners, is set up. The drilling dust appears to be more harmful in its effect than the blasting dust, but no significant differences between the two could be discovered by ordinary methods. The electron microscope was used to examine the dusts and to determine whether any important differences did exist.

The established method at this laboratory for the determination of particle sizes in aerosols by the electron microscope consists at the present time of the following procedure.   The particles of the dust are mounted from a cloud by means of a thermal precipitator (5).   This apparatus was used originally to collect particles for light microscope examination, but, by adapting it, it can be used to secure deposits directly upon the collodion film of an electron microscope specimen holder.   This adaptation consists of cutting a depression 0.01 cm. deep and 0.3 cm. in diameter at the centre of the usual thermal precipitator plug.   The mesh with attached film is fastened into the depression with rubber cement.   These plugs with the holder attached can be used in the thermal precipitator *in the mine* in order to collect specimens of the dust *as it occurs in the air*.

A series of electron micrographs are taken over the width of the thermal precipitator deposit, for several positions along its length.

From these photographs, projected on a screen at ×50,000 (5.0 cm. = 1 μ), the particle sizes can be measured easily and the numbers in any particular size range can be counted.   From the data obtained in this way a graph has been plotted of the diameter of the particles versus the percentage in a chosen range (Fig. 7).

From these experiments it was concluded that the percentage of particles with diameters less than 0.20 μ was much greater in the drilling than in the blasting dust.   About 50% of the particles in the drilling dust were less than 0.10 μ in diameter; about 12% of the particles from the blasting dust were of a smaller size.   Optical microscope counts made by Dr. Beatrice R. Deacon, of samples taken on light microscope slides at the same time as the electron microscope samples were obtained, gave good correlation in the range 0.10 to 2.0 μ.   The distributions of the dusts were very asymmetrical.

Fig. 8 is a representative view of the large particles present in the blasting dust.   Fig. 9 illustrates the finer material in the drilling samples.

An attempt was made to mount dust that had been collected by a carpet sweeper in the mine.   This proved impractical because of the general aggregation of the particles.

In the samples that yielded the results already described, there must have been a certain amount of material that was not silica.   Unfortunately some debris is always present in the air and is mounted along with the silica.   In the experiment described, no attempt was made to remove it.   Heat and acid treatment have been suggested but neither is as yet practical.   In securing the above distribution those particles that were manifestly not silica were left uncounted.

The use of the thermal precipitator as a piece of standard equipment for mounting aerosols for electronic investigation is an important mounting technique, especially when a good distribution of the particles under the conditions in which they *normally occur in the air* is desired.
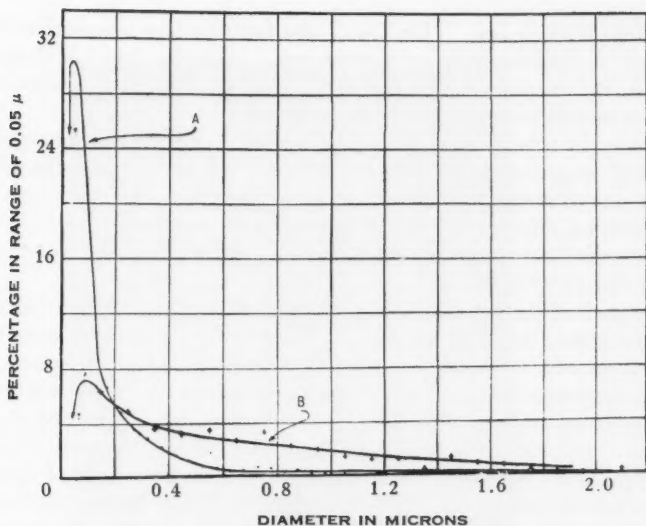
FIG. 7. *A graph showing the relation between the diameters of the mine dust particles measured in microns and the percentage of the particles in ranges of 0.05 μ for both the blasting and the drilling dusts. A, drilling dust; B, blasting dust.*

The Use of the Electron Microscope as an Electron Diffraction Camera

Electron diffraction technique is easily adapted to a modern electron microscope (4). In the Toronto instrument, at present, the limiting aperture of the projector lens is too narrow to allow electron diffraction patterns to be secured unless the projector lens and the central chamber joining the objective and projector lenses are removed. With the instrument set up under these conditions, photographs can be taken at a magnification of ×100 and electron diffraction patterns can be obtained of the same sample. The patterns can be improved by using the original objective lens of the microscope as a weak supplementary lens.

There are two possible positions for the object. It can be located below the projector or above the objective lens. Each location has inherent advantages, and in order to profit from all of them it should be made possible to locate the object in either position for examination by electron diffraction technique.

Hillier (4) has devised a combination of a projector lens and a very weak supplementary lens to which the name, electron diffraction adapter, has been given. The object is inserted between the lenses. The projector lens current is zero when the adapter is functioning and the supplementary lens is used for focusing the diffraction pattern. For any given voltage there is an optimum value for the supplementary lens current for which the definition

of the rings is at its best.   The use of this focusing lens is a worthwhile improvement for electron diffraction technique.   With the object in the position indicated, the operator has good control over the object and is able to take reflection as well as transmission photographs.

However, in this position it is not possible to obtain a micrograph of the sample; a specimen must be removed from the position below the projector lens and placed in the object chamber above the objective.   Although in this new position a micrograph of high magnification can be obtained, it is very difficult to pick out the same field of view as that which produced the diffraction pattern with the adapter.

On account of the fact that the instrument cannot be used as a microscope when the object is below the projector, it is not possible to examine the specimen in order to choose a particular fragment of it for investigation.

If the specimen is located above the objective lens, a larger diaphragm is necessary in the objective and a special camera assembly is needed above the projector.   It is not possible to manipulate the specimen as easily and reflection patterns are not obtainable.   By improved designs, both of these difficulties might be overcome.   However, with the object so placed it is possible to secure micrographs at high magnification of the *same* area of the specimen as is producing the pattern, and consequently the specimen can be examined microscopically in order to choose a particular fragment of material to produce the electron diffraction rings.   Using a very fine electron "probe" it is possible to examine single small crystals, or small fibre fragments that are thought to possess orientation.

It has been found that the collodion and Formvar films, on which electron microscope samples are mounted, themselves produce very broad, diffuse diffraction rings by transmission.   These rings tend to lower the contrast in certain areas of the diffraction pattern, but they are easily recognized and are not to be confused with those formed by the crystal sample itself.

It is a very happy circumstance that the electron microscope system can be adapted in a relatively simple way for either microscope or electron diffraction investigations.   The two processes are complementary and information not provided by the one can often be secured by use of the other.   The electron *micrograph* presents information concerning the size, the shape, and the relative abundance of the material in the specimen.   The electron *diffraction pattern* can offer data related to crystal structure in the *same* specimen. It can be used to determine quantitatively the crystal properties of the sample and to decide whether or not there is definite orientation in its structure.   Electron diffraction methods can be used to examine very small quantities of material and it is possible to line up the electron beam in order to direct it against definite minute areas of the specimen.   The technique of electron diffraction has been greatly advanced by Prebus.

The combined use of the electron microscope system can be illustrated in the following investigation of clay samples.   The problem was undertaken in order to examine the size and shape of the crystals of a Canadian clay in

PLATE III
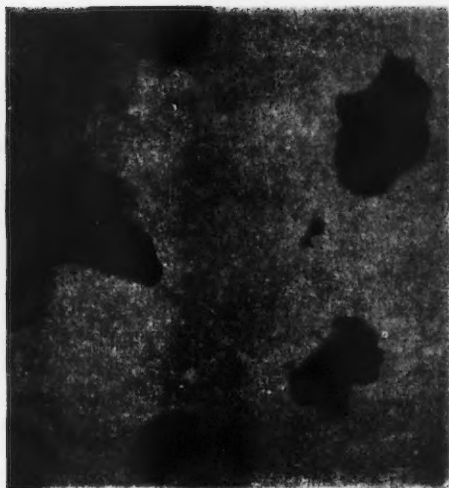
FIG. 8

FIG. 9

FIG. 8. *Electron micrograph taken of mine dust collected after blasting operations.* ×16,100.
FIG. 9. *Electron micrograph taken of mine dust collected after drilling operations.* ×16,100.

PLATE IV
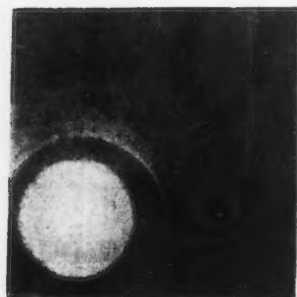
FIG. 10 A

FIG. 10 B

FIG. 11 A
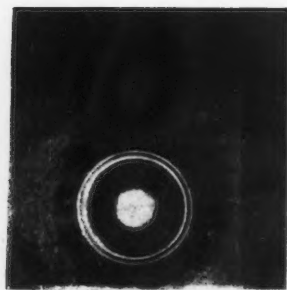
FIG. 11 B

FIG 10A. *An electron micrograph of a Cornwall paper coating clay.* $\times 11,400$. FIG. 10B. *The electron diffraction pattern produced by this clay.* FIG. 11A. *An electron micrograph of titanium oxide particles also used in paper coating.* $\times 15,300$. FIG. 11B. *The electron diffraction pattern produced by the titanium oxide.*

order to compare them with those of English and American clays. To a certain extent the project was initiated by those interested because of the difficulties in transporting clays from other countries during the war. Large quantities of these clays as well as other material to be mentioned are used for coating paper.

The same "platelet" crystals were present in each of the samples of Canadian, American, and English clays photographed. The Canadian clay seemed to compare favourably with the others as far as the electron micrograph was able to show. The hexagonal platelet form of the crystals, their general size range and their abundance could be deduced from the micrograph. Fig. 10*A* is a typical micrograph. It represents a section of a sample of the English Cornwall clay. Fig. 11*A* shows a distribution of titanium oxide particles also used in paper coating.

All these clay samples demonstrate the same lines in their electron diffraction patterns, and would appear to be composed of the same crystalline material of somewhat the same size. Intensities of the rings have no meaning as far as interpretation is concerned because in order to print the pictures they have to be shaded. The centres of the actual negatives are very dark compared with the outer areas owing to the large number of electrons that are scattered at small angles.

Fig. 10*B* is the diffraction pattern formed by the sample of Cornwall clay. The other samples formed similar patterns. Fig. 11*B* shows the pattern formed by the sample of titanium oxide. The rings formed by the supporting Formvar film have been shaded out as much as possible in the printing.

II. APPLICATIONS OF THE ELECTRON MICROSCOPE TO BOTANICAL INVESTIGATIONS

Cuticle from the Leaf of *Antirrhinum majus* L. var. *Rosalie*

Under the superficial wax covering of leaves is found the outer structural layer known as the cuticle, which is made up of a fatty substance known as cutin. The cuticle has been generally regarded as water-impermeable but recent evidence (1, 6) indicates that this is not so. This study was undertaken to discover whether the electron microscope could demonstrate either the existence of holes in the cuticle or some other factor that would indicate the permeability of the cutin.

In cut sections of leaves the cuticle can be optically demonstrated by the use of standard staining techniques but such methods are not possible with the electron microscope. It was decided to attempt to mount the cuticle *as a film*. Leaves were taken from the snapdragon (*Antirrhinum majus* L. var. *Rosalie*), the surfaces of which are characterized by numerous stomata.

The specimens were prepared in the following way. Two or three leaves were treated with butyl acetate to dissolve the waxy, surface substances. The butyl acetate was washed away with 50% alcohol and the leaves were subjected to the action of 72% sulphuric acid (cold) for half an hour. The

acid was next heated carefully until the leaves began to "fall apart". During this process all the leaf except the cutin is digested. The cuticular layer is unaffected and is left as a fairly clean, thin sheet.

The surplus acid was removed and the rest of the material was poured into a large beaker of water. The thin sheets of cutin floated on the surface and were easily mounted across the electron microscope holders as a film. The dried film was drawn tightly across the holes in the mesh; it did not crease.

As the age of the plant increased, new samples were prepared and photographed. In Plate V are several micrographs of the cutin film mounted from samples prepared on successive dates.

Fig. 12A shows the cutin to be a thin, structureless, transparent film. It becomes definitely fibrous as time goes on, as in Fig. 12B where the membrane has cracked under the tension. The older leaves require a more vigorous treatment in order to secure thin enough membranes. A fairly thick cutin film is shown in Fig. 13A. It is uneven in thickness and constitutes a *replica* of the upper surface of the first layer of cells in the leaf. The thicker areas represent the portions of the cuticle that were directly above the positions of cell division. Fig. 13B shows the presence of undigested vascular tissue in a sample of cutin from an older leaf (even after vigorous treatment). In the final picture, Fig. 13C the cutin is exceedingly thick and fibrous, again constituting a replica of the upper surface of the upper cells of the leaf.

The presence of holes is not detected in any photograph. In Fig. 12B the cutin is shown to be composed of several fibrous layers, the fibres having a width of about 0.08μ. If the number of layers is sufficient the cuticular film appears to be homogeneous and structureless. This is its usual appearance. The cutin being fibrous will consequently be permeable, its permeability depending upon the closeness of the fibre weaving and upon the number of layers. It is to be expected that the covering of a younger leaf with fewer thicknesses of cutin will be more permeable. The outer wax covering also affects the permeability of the leaf surface.

The Wall Structure of the Mesophyll of *Aloe arborescens* Mill.

An incomplete study of the wall structure of the mesophyll of leaves of *Aloe arborescens* Mill. is reported here. The mesophyll cells are the water storage cells whose walls are composed chiefly of hemicelluloses, which contain considerable water and shrink if put into alcohol or other drying agent. The hemicelluloses comprise all the cellulose-like carbohydrates of the outer cell layers and are very easily hydrolysed in comparison with ordinary cellulose.

The walls were treated in three different ways and were photographed by the electron microscope after the treatments. The results are inconclusive but the micrographs are offered as an attempt to study the cell wall and the changes produced in it by the three treatments.

1. A quantity of the mesophyll was left for a few minutes in concentrated copper sulphate solution and then treated for three hours in 50% potassium

PLATE V

X 2600   A   B   X 1500

FIG. 12

X1700   A   X1900   B   X1900   C
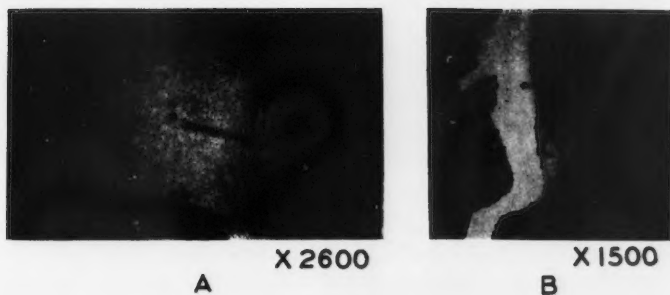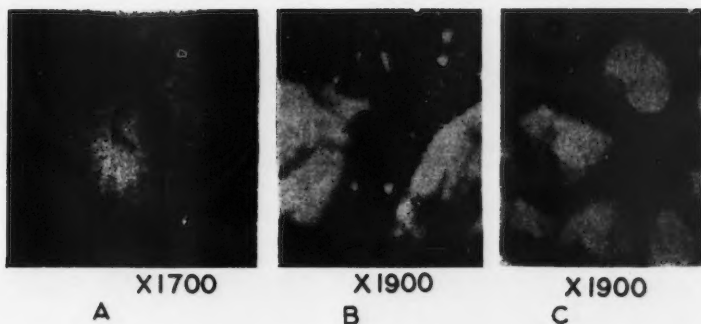
FIG. 13

FIG. 12A. *Electron micrograph of the earliest sample of cutin mounted as a film.* ×2600. FIG. 12B. *Electron micrograph of the cutin film taken from an older plant. The fibrous nature is beginning to be evident.* ×1500. FIG. 13A. *Electron micrograph of cutin film taken from a section of the surface where the cutin was immediately above the position of cell division and the cutin constitutes a "replica" of the upper surface of the outer cells of the leaf.* ×1700. FIG. 13B. *Undigested vascular tissue in the leaf.* ×1900. FIG. 13C. *A very old leaf in which the cutin is quite fibrous and thick. The cutin again constitutes a "replica".* ×1900.

PLATE VI
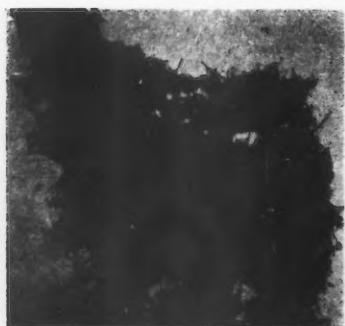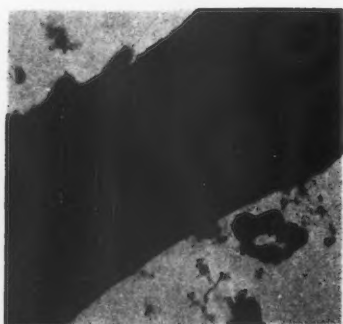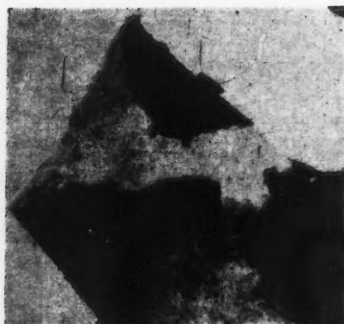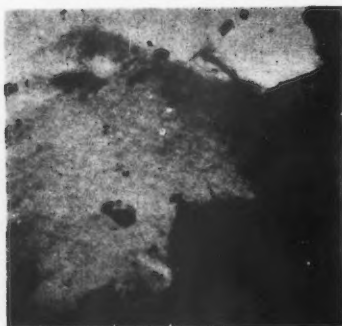
FIG. 14A. Electron micrograph of the mesophyll of the aloe after the treatment with copper sulphate and potassium hydroxide. ×3170. FIG. 14B. Same as A. ×3410. FIG. 15A. Electron micrograph of the mesophyll of the aloe after it had been ground under liquid air and resuspended in water. ×3460. FIG. 15B. Same as A. ×3460. FIG. 16A. Electron micrograph of the mesophyll of the aloe after treatment with hydrochloric acid and ammonium hydroxide. ×3300. FIG. 16B. Same as A. ×3030.

hydroxide solution. The resulting material was washed and photographed. The structure shown in Figs. 14*A* and 14*B* is very fibrous, part of the wall appearing to be quite cloth-like. This is apparently wall material from which some of the binding pectic materials have been dissolved. In places the wall seems to be in a less decomposed state but it is riddled with holes. The fibres are about 0.08μ in width.

2. A quantity of the mesophyll was boiled in distilled water for a half hour and left to swell in the water for some days. It was then ground under liquid air, resuspended in water and mounted for examination. Figs. 15*A* and 15*B* show some of the cell content as well as sections of the wall that are apparently homogeneous and still cemented together firmly with pectic materials.

3. A quantity of the fresh cell wall was heated in hydrochloric acid for an hour at 90° C. in an attempt to remove the binding materials. The residue was washed and treated with ammonium hydroxide for 15 min. at the same temperature. It was again washed and prepared for the electron microscope. Figs. 16*A* and 16*B* show two sections of the wall. In Fig. 16*A* the binding materials have been partially dissolved, the wall structure has been loosened, and its essential nature is seen to be fibrous. (Note also the structure visible in a vascular fragment indicated by an arrow.) In Fig. 16*B* the wall still presents a fairly homogeneous appearance.

These results indicate that fine fibrous structures are present in the remains of the hemicellulose walls after chemical treatment. The evidence would be more satisfactory if the true chemical nature of these fibrous remains and their position in the original cell wall could be positively stated. Botanists themselves regard the nature of the chemistry of the cell wall and its changes under treatment as extremely difficult to determine.

Stereoscopic Views of Broken Flax Fibres

Flax fibres were broken up in a Waring blendor and specimens were prepared for the electron microscope. The photographs shown in Fig. 17, *A* and *B*, are stereoscopic views of the broken fibres. The cell wall is apparently extremely thin, judging by its lack of resistance to the electron beam. Many fine fibrils are visible in the background of the photographs. Their widths range from about 0.6 to 0.06μ. The significance of these fine fibrils in the structure of the main fibre is not immediately evident. The absorption of electrons is not the same as that due to the wall; the fine fibres do not seem to be a part of the wall. The broken flax was mounted from a water suspension.

The Place of the Electron Microscope in Botanical Research

Plant cells and whole fibres are too large and thick to be studied directly by the electron microscope. Cell walls or component parts of fibre structure are more amenable to electronic investigation, but they must be broken up either chemically or mechanically. Once the wall has been so treated and

photographed it is very difficult to say how the structure observed in the micrograph is arranged in the original untreated specimen.

Any material with minute structure (less than $0.3\,\mu$) such as is found in a diatom shell can be studied to advantage with the electron microscope (2, 3).

A great many electron micrographs have been taken, at this laboratory and elsewhere, of samples of cotton fibres prepared in diverse ways. But in the study of the wall structure of cellulose the same difficulties enter regarding the interpretation of the original wall from the micrographs. Fibrillated structures appear to be very interesting. From X-ray experiments it is known that there is a well defined crystal structure in cellulose, and the polarizing microscope shows that the crystals are definitely oriented. The electron microscope appears to be one of the most promising instruments for studying the size and shape of the micelles, their arrangement in the fibrils, and the arrangement of the fibrils in the whole fibre.

The electron microscope may be applicable to the study of the structure of chromosomes. It is true that chromosomes would dry in the vacuum of the instrument and that their structure might undergo changes under these conditions, but regardless of the difficulties, such an electron microscope investigation would be important and would reward any real effort expended in its pursuit.

Applications of the instrument to botany involve considerable time, experimentation, and a good knowledge of the materials so that they may be prepared in such a way as to take full advantage of the high resolution of the electron microscope. When suitable methods of preparation are developed, considerable study of botanical specimens will be worth while.

Acknowledgments

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PLATE VII

X1200

A
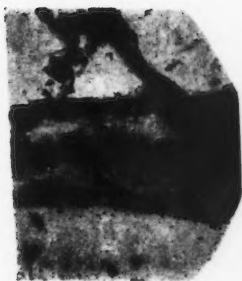
X1200

B

FIG. 17A. *Stereographic view of flax fibres broken up in a Waring blendor.* ×1200.
FIG. 17B. *Same as A.*
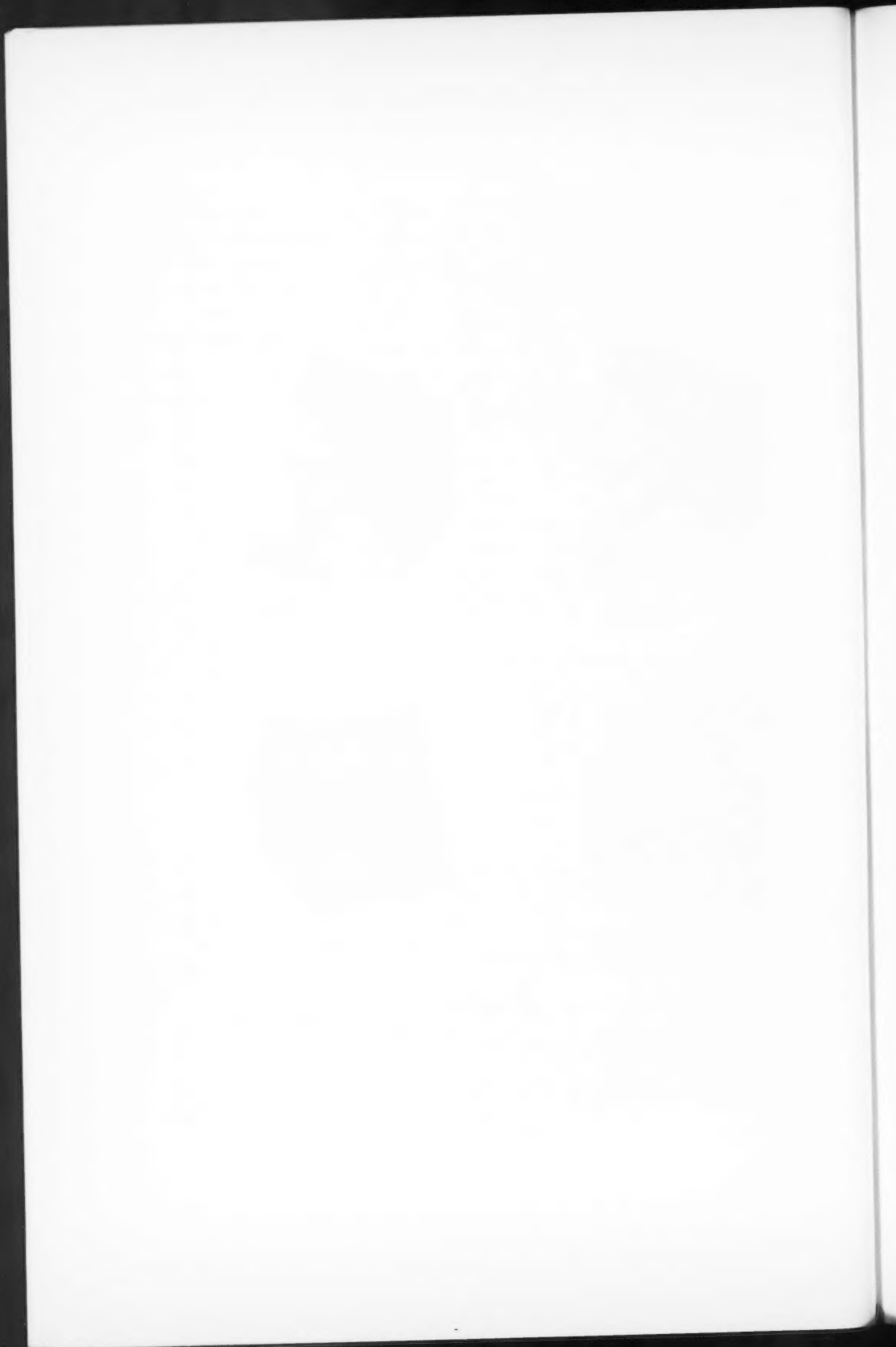
SURFACE TENSION OF SODIUM SOAP DISPERSIONS IN MINERAL OILS[1]

BY WILFRED GALLAY[2] AND IRA E. PUDDINGTON[2]

Abstract

The surface tension of sodium stearate and sodium oleate dispersions in mineral oils of high and low viscosity index has been measured over a wide range of temperature. In dispersions in the non-polar oil, no surface activity is shown by the soap until the full melting point is reached. In dispersions in an oil of relatively high polarity, surface activity is shown at much lower temperatures corresponding to partial melting points of the soaps. The ability of the soap to lower the surface tension is dependent on the degree of dispersion of the soap, and the relation of surface activity to physical states and phase transitions, previously determined by the authors, is discussed. The addition of glycerol increases the surface activity at a given concentration, but the temperature at which surface activity is attained remains unaffected. Excess fatty acid acts similarly to glycerol; excess alkali decreases surface activity.

No data have hitherto been available in regard to the surface tensions of dispersions of soap in organic media other than alcohol. Such data are of interest not only in connection with the surface activity of soaps in such systems, but also in their relation to the problem of the physical states and phase transitions in these soaps. A number of measurements of static surface tensions of soaps in mineral oils were carried out over a range of temperature, a capillary rise method being used.

Fig. 1 shows graphically the results obtained in a non-polar oil of 95 V.I. The surface tension of the oil alone decreases linearly with temperature. There is no lowering of the surface tension of the soap dispersion until a temperature of about 140° C. is reached. The introduction of the glycerol has no effect on the temperature at which surface activity is attained, but causes a decrease of about 2.5 dynes, as compared with a decrease of about 1 dyne for the soap without glycerol. In each case, after the sudden decrease in surface tension, the thermal coefficient remains the same as for the oil alone, denoting a stable phase over the interval measured.
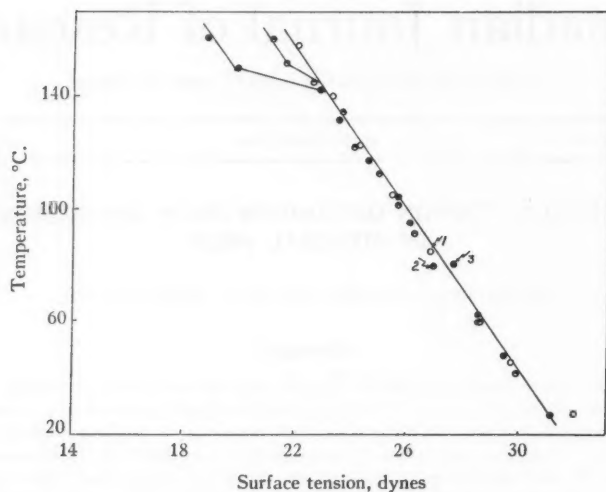
FIG. 1. *Surface tension of sodium oleate in a non-polar oil. 1, oil alone; 2, sodium oleate dispersion; 3, sodium oleate dispersion together with glycerol.*

Fig. 2 shows graphically the results obtained with sodium oleate in a polar oil of about 40 V.I. The surface tension of the oil alone decreases linearly with temperature and the thermal coefficient is essentially the same as that of the non-polar oil. A sharp decrease in surface tension is obtained with
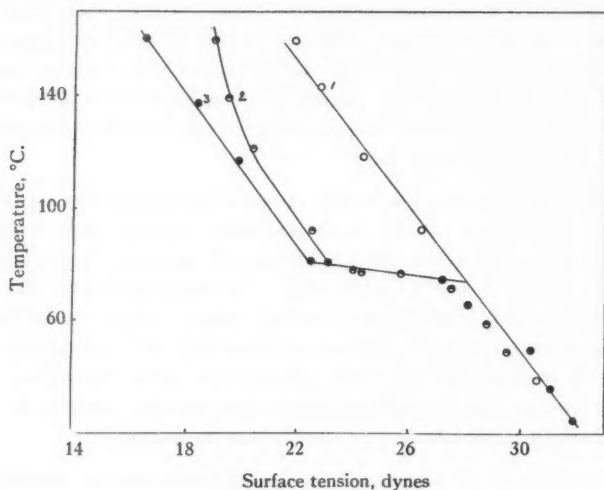
FIG. 2. *Surface tension of sodium oleate in a polar oil. 1, oil alone; 2, sodium oleate dispersion; 3, sodium oleate dispersion together with glycerol.*

the 1% soap dispersion at about 75 to 80° C. The addition of glycerol to this dispersion results in a surface tension decrease at the same temperature, but the extent of lowering is appreciably increased in the presence of the glycerol. The surface tension decrease is about 4.0 and 4.5 dynes for the soap and soap–glycerol dispersions, respectively.

Fig. 3 shows graphically the results obtained with sodium stearate in a polar oil of about 40 V.I. A 1% dispersion of the soap shows a lowering of surface tension at some temperature intermediate between 95° and 108° C. No further data are available covering this interval. The addition of glycerol to this soap dispersion results also in a decrease at about 100° C. This would
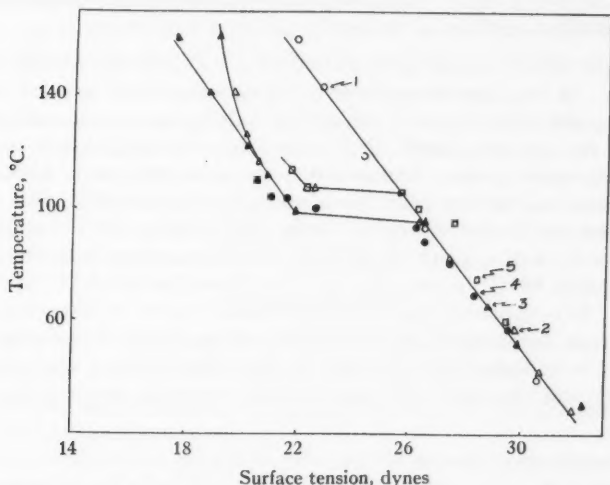
FIG. 3. *Surface tension of 1% sodium stearate in a polar oil. 1, oil alone; 2, sodium stearate dispersion in oil; 3, sodium stearate dispersion in oil with 30% glycerol based on the soap; 4, sodium stearate dispersion in oil with 10% free fatty acid based on the soap; 5, sodium stearate dispersion in oil with 2.5% free alkali based on the soap.*

indicate that the temperature at which surface activity is attained in the soap dispersion without glycerol is also at about 100° C. Much the same effect was produced also by the addition of fatty acid to the soap dispersion. The addition of alkali to the soap resulted in a somewhat higher temperature of surface tension lowering, about 105° C., and the extent of the lowering was appreciably reduced.

Discussion

The interpretation of surface tension data of soap dispersions in water has been vastly complicated by ionization and attendant effects. It is not known, for example, whether the surface-active constituents are solely unaggregated single ions, or large ionic micelles, or particles of intermediate size. The

concentration of highly dispersed particles is dependent not only on concentration but also on the presence of very small amounts of excess alkali or fatty acid. Dispersions of soaps in a medium of low dielectric constant, however, present a much simpler picture.

The present work shows clearly that the surface activity of the soap is closely related to its physical state. A non-polar mineral oil has been shown (2) to have no effect on the physical state of the soap below the temperature at which the polar bonds of the soap lattice are disrupted. A sodium soap in such a medium is shown in the present work to possess no surface activity until the full melting point (1) up to the liquid–crystalline state has been reached. Surface activity of the soap is therefore dependent on the dispersion of the crystallites resulting from the disruption of the lattice.

The suspensions in a polar oil of relatively low V.I. show a markedly different behaviour. It has been shown previously (2) that such a polar addition agent is capable of acting as a solvent for sodium soaps once sufficient disruption of the non-polar bonds of the soap lattice has taken place as a result of the application of heat. The solubility becomes particularly marked after the bidimensional melting point (1) of the soap has been reached. Sodium stearate becomes surface active in a polar oil at about 100° C., which is the bidimensional melting point of the soap. Sodium oleate becomes surface-active at about 80° C. in the polar oil, as compared with 140° C. in the non-polar oil. It is apparent that a certain definite degree of disaggregation of the soap must be attained before surface activity can be manifested by the material. It appears likely that the double molecule form that obtains in the soap crystal (3) must be disrupted for the necessary concentration at the interface.

The neutralization number of this polar oil is 0.28, which shows an appreciably larger free acid content than the non-polar oil (neutralization number, 0.04). It has been previously shown however (2) that these small quantities of free acids can have no significant effect on the physical state of the soap until the region of complete melting is approached. The effect obtained with the polar oil is therefore to be ascribed to the chemical nature of the oil constituents and not to the small amounts of free fatty acids contained.

The addition of glycerol in 30% concentration based on the soap has no effect on the temperature at which surface activity is attained. The extent of the lowering of the surface tension is, however, increased by the glycerol, which must act in the direction of an increase in the degree of dispersion of the soap. It is noted that in the absence of glycerol, a reversion towards a higher surface tension is obtained with both sodium stearate and sodium oleate at higher temperatures. In the presence of glycerol, the linearity of the surface-tension–temperature relation is maintained. Excess fatty acid acts similarly to glycerol in increasing the surface activity without altering the temperature at which the lowering of surface tension is obtained. Excess

alkali not only decreases surface activity but raises the temperature of surface tension decrease. This reagent was shown to have a corresponding effect on the physical state of the soap (2). It is interesting to note that sodium stearate and sodium oleate show the same degree of surface activity at the concentration used, after dispersion of the soap had been effected in each case.

In the case of the sodium-oleate–glycerol dispersion in the 95 V.I. oil, the system was shown to be reversible; the surface tension values obtained after cooling were the same as those measured for the suspension prior to heating.

Experimental

The oils used had a viscosity of about 900 S.U.S. at 100° F. in each case, and the viscosity indices were about 95 and 40 for the high and low V.I. oils, respectively. Inspection data for these oils were given in a previous paper (2).

A capillary rise method was used for the determination of surface tensions. The diameter of the arms of the U-tube were 2.9 and 0.0395 cm., and experiments were carried out in an oil thermostat. The apparatus was calibrated with distilled water, the error in several determinations being of the order of $\pm$ 0.25%. The usual precautions were taken with regard to attainment of equilibrium. Densities of the systems were measured in a pycnometer, using the same thermostat at the temperature required.

Acknowledgment

References

1. GALLAY, W. and PUDDINGTON, I. E. Can. J. Research, B, 21 : 202-210. 1943.
2. GALLAY, W. and PUDDINGTON, I. E. Can. J. Research, B, 21 : 211-218. 1943.
3. THIESSEN, P. A., STAUFF, J., and WITTSTADT, W. Angew. Chem. 49 : 640-642. 1936.

WETTING POWER IN SODIUM-SOAP—MINERAL-OIL SYSTEMS[1]

By Wilfred Gallay[2], Ira E. Puddington[2], and James S. Tapp[2]

Abstract

Measurement of the contact angle of various mineral oils on surfaces of sodium soaps showed no appreciable variation with oils of varying polarity. Low V.I. oils show a lower interfacial tension against water, and greater emulsion stability. Mineral oils possess high spreading power on soap surfaces previously wet with glycerol. As a result, mineral oils are rapidly absorbed by a soap–glycerol gel, and at the same time the glycerol is displaced and forced out of the gel. Data are shown for some quantitative measurements of this preferential wetting action, various oils and elevated temperatures being used. These experiments are extended to sodium soap base lubricating greases, and the presence of free glycerol is demonstrated in such systems where fats were used in the manufacture of the grease.

Wetting Power

Sodium soaps are in general poorly wetted by mineral oils, and it was of interest to determine the effect of the polarity of the oil, as represented by its viscosity index, on the degree of wetting obtained. Advancing contact angles were measured by a drop method on melted and pressed soap surfaces. A melted soap surface was prepared by melting the soap on a microscope slide and spreading it to a uniform sheet while still hot. Pressed soap surfaces were prepared by heating the soap in a pellet mold to about 100° C. and then pressing the soap under high pressure. The contact angle measurements were made on the relatively non-polar soap surfaces, i.e., the surfaces that had cooled in contact with air. Table I shows the results obtained, each figure being an average for several determinations.

It is apparent from these data that the V.I. of the oil has little effect on the relatively non-polar soap surface as judged from these contact angles. In all cases the presence of glycerol brought about a decrease in contact angle and sodium stearate was more readily wet than sodium oleate. The viscosity of the oil has an appreciable effect.

Interfacial Tensions

The interfacial tensions between an aqueous soap dispersion and a mineral oil should show some variation with the polarity of the mineral oil. The interfacial tensions measured were, however, so low as to render impossible the detection of such differences by ordinary means. In the case of interfacial tension between oil and water, an oil of 40 V.I. yielded a tension some 5 dynes less than an oil of 95 V.I. There is therefore an important concentration of polar constituents at the interface.

TABLE I

CONTACT ANGLES OF OILS ON SODIUM SOAPS

Soap	Oil	Contact angle, degrees
A. Melted soap surfaces		
Neutral sodium oleate	900 vis. 95 V.I.	50.7
	900 vis. 40 V.I.	49.2
	100 vis. 95 V.I.	45.2
	100 vis. 40 V.I.	43.0
Neutral sodium stearate	900 vis. 95 V.I.	45.7
	900 vis. 40 V.I.	44.5
	100 vis. 95 V.I.	40.5
	100 vis. 40 V.I.	37.0
Sodium stearate (10% F.F.A.) + 10% glycerol	900 vis. 95 V.I.	41.0
	900 vis. 40 V.I.	42.2
	100 vis 95 V.I.	34.7
	100 vis. 40 V.I.	33.7
B. Pressed soap surfaces		
Neutral sodium oleate	900 vis. 95 V.I.	52.4
	900 vis. 40 V.I.	51.1
	100 vis. 95 V.I.	48.0
	100 vis. 40 V.I.	46.1
Neutral sodium stearate	900 vis. 95 V.I.	40.0
	900 vis. 40 V.I.	40.0
	100 vis. 95 V.I.	35.0
	100 vis. 40 V.I.	36.0

The stability of oil-in-water emulsions was found to vary with the V.I. of the oil, using sodium oleate as emulsifying agent. Oils of 40 V.I., particularly those of higher viscosity, yielded stable well dispersed emulsions, whereas the corresponding 95 V.I. oils yielded emulsions that broke much more readily. It was found further that there was no appreciable difference in speed of demulsification where no soap was used, and therefore most of the differential action of the oils is on the soap in maintaining the protective action required.

The Effect of Glycerol on Surface Relations Between Sodium Soaps and Mineral Oils

Glycerol is of particular interest in these soap–oil systems because of its importance in the preparation and resultant properties of sodium soap lubricating greases.

As noted above, if a drop of a mineral oil is placed on a soap surface, it shows little tendency to wet and spread. Glycerol, on the other hand, wets the soap surface quickly and the spreading tendency is very marked. If now a drop of the same mineral oil is applied to a soap surface previously wet with glycerol, then it is found that the oil wets the surface quickly and the spreading tendency is very great. It has already been shown (1) that glycerol cannot

exert any solvent action on a sodium soap crystal at room temperature. Furthermore, glycerol is insoluble in the mineral oil, as is also the soap. It would appear that the explanation of the action of the glycerol may be that the glycerol, in being adsorbed on the soap, alters the nature of the soap surface so that the composite surface can then be wet by the oil. Glycerol may be regarded as dipolar through its short hydrocarbon chain and polar hydroxyl groups. There is therefore an opportunity for the alteration of the soap surface to one that is essentially non-polar and that can then be wet by hydrocarbons.

In this connection the following observation is of interest. A drop of glycerol dropped on to an oil–water interface adhered to the interface, and solution into the water was remarkably slow. It was then found as a result of the introduction of glycerol into the interface that the interfacial tension was reduced by about 7 dynes, a rather surprising decrease in view of the fact that glycerol has no effect on the surface tension of water at these low concentrations. It was noted however that the glycerol was readily removable from the interface by mild agitation, and a corresponding effect was obtained on the interfacial tension. The initial concentration at the interface was probably high. This effect of glycerol is undoubtedly analogous to that noted on a soap–oil interface.

The investigation was then extended to soap blocks containing various large amounts of glycerol, prepared by heating a mixture of soap and glycerol to the point of apparently complete solution and then allowing the mixture to cool in a mold. It was found when such mixtures were wet with mineral oil, say by partial immersion, that large quantities of oil were absorbed by the soap. At the same time it was found that glycerol was set free from the mixture, and further that the quantity of oil absorbed was equal to the quantity of glycerol set free. Fig. 1 shows drops of glycerol that exuded from a 50% soap–glycerol gel after a brief interval of partial immersion in a mineral oil.

The quantitative relations involved are of interest, particularly the maximum extent of glycerol removal. It is apparent that an actual displacement of the glycerol by the oil takes place. A number of preliminary experiments using relatively thick pellets of soap–glycerol gel yielded inconclusive results, since the glycerol set free was allowed to remain within the pellet and was therefore analysed as unremoved. In subsequent experiments the soap–glycerol blocks were placed in a microtome and sections some 0.2 mm. thick were cut off. These sections were then immersed in various oils for varying periods. After exposure, analysis was carried out for soap and glycerol in the soap block. Table II shows the results after varying periods at 75° C. The following mineral oils were used:

No. 1.   100 vis. 40 V.I.
No. 2.   900 vis. 95 V.I.
No. 3.   900 vis. 40 V.I.
No. 4.   100 vis. 95 V.I.

PLATE I

FIG. 1
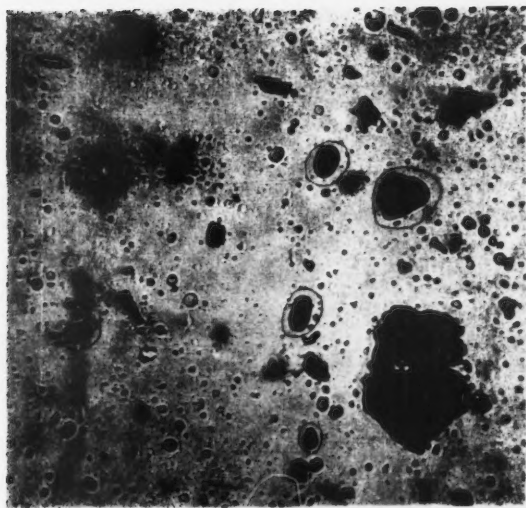
FIG. 2

FIG. 1.   *Displacement of glycerol from a soap–glycerol gel by mineral oil.*

FIG. 2.   *Photomicrograph showing free glycerol in a sodium soap grease.*
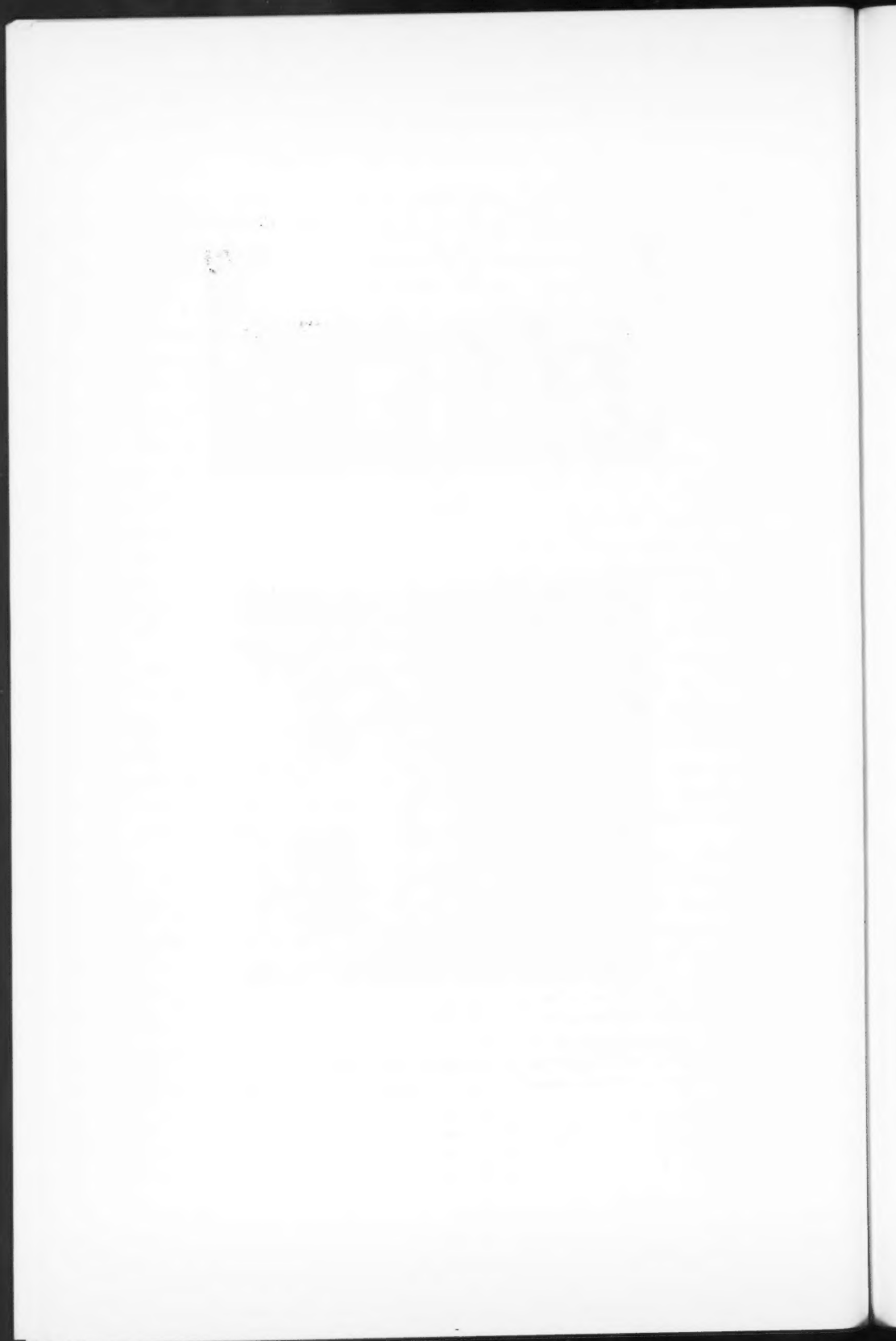
Analysis of the original soap–glycerol gel gave a total for these constituents of 93.6%. The remaining 6.4% is presumably water since it is difficult to obtain completely anhydrous soap and glycerol. The figures for percentage oil in Table II were obtained by subtracting the sum of the percentages of glycerol and soap from 93.6%. This water content may decrease as glycerol is removed, so that the oil/soap values for the longer times are probably slightly low.

TABLE II

DISPLACEMENT OF GLYCEROL FROM SOAP–GLYCEROL GEL BY MINERAL OILS

Time of immersion	Oil No.	Composition of soap gel				
		Soap, %	Glycerol, %	Oil, %	$\dfrac{\text{Glycerol}}{\text{Soap}}$ %	$\dfrac{\text{Oil}}{\text{Soap}}$ %
0	—	46.0	47.6	—	103	—
1 min.	1	38.9	13.9	40.8	36	105
	2	41.9	23.2	28.5	55	68
	3	42.3	23.1	28.2	55	67
	4	39.5	12.0	42.1	30	107
8 min.	1	37.4	10.5	45.7	28	122
	2	41.1	10.2	42.3	25	103
	3	39.7	10.2	43.7	26	110
	4	39.1	10.7	43.8	27	112
30 min.	1	34.6	9.7	49.3	28	143
	2	40.5	10.1	43.0	25	106
	3	38.8	9.5	45.3	25	117
	4	37.2	10.2	46.2	27	124
90 min.	1	37.0	9.8	46.8	27	127
	2	39.3	9.7	44.6	25	113
	3	39.8	9.4	44.4	24	112
	4	34.1	10.0	49.5	29	145
21.5 hr.	1	35.0	9.4	49.2	27	141
	2	38.4	9.2	46.0	24	120
	3	37.8	8.0	47.8	21	127
	4	36.0	9.2	48.4	26	134

It is noted that here, also, oil is taken up by the soap, and glycerol is displaced from the gel. The same relations hold as noted above for oil on a soap–glycerol surface. The wetting and displacement are rapid, and equilibrium is attained within an 8 min. period for the soap gel sections 0.2 mm. thick. The column in Table II showing the percentage glycerol in the gel based on the soap is the best indication of the course of the changes that have occurred. It is noted that there is little difference among the four oils used and that in the systems used an equilibrium appears to have been reached with a residue of about 25% glycerol based on the soap. The low viscosity

oils show much more rapid penetration, as might be expected.   The V.I. of the oil has no effect on the magnitude or speed of glycerol removal; this might be expected since the soap is already saturated with material of a polar nature.   The amount of oil held by the soap also reaches an approximate equilibrium within a short period of time.

It was of particular interest to extend these experiments to systems containing soap in very finely dispersed form.   The use of fats in the manufacture of sodium soap base lubricating greases is common, and it is known empirically that the presence of glycerol due to the use of fats for the soap preparation results in certain desirable physical characteristics in the grease.   In large scale industrial procedure, the ingredients are heated until the system is homogeneous and then the soap–glycerol–oil dispersion is allowed to cool under certain definite conditions.   It would appear that here also the displacement phenomena described above should take place.   The glycerol set free should then be present as droplets in the oil.   Since these droplets are not directly visible, owing to refractive index considerations, the following method was used to demonstrate their presence.   To a thin layer of sodium soap lubricating grease manufactured from fat, there was added a small quantity of finely divided methylene blue dye.   This was spread lightly over the grease and allowed to mix.   Microscopic examination then showed coloured areas of (i) irregular shape and (ii) spherical or ovoid shape with smooth contour.   The latter appeared after standing for 24 hr.   The irregularly shaped particles are obviously a suspension of the water-soluble dye in the oil.   The spherical or ovoid shapes must however represent droplets of glycerol dyed preferentially by the methylene blue.   Fig. 2 shows an example of a photomicrograph in which a few of such droplets of glycerol are indicated by means of light lines drawn around them.

A number of sodium soap base greases were investigated in this regard. It was found without exception that those greases that had been prepared from fats and alkali, i.e., containing glycerol, showed these free droplets of glycerol.   On the other hand, all those sodium soap base greases prepared from fatty acids and alkali, i.e., containing no glycerol, showed no trace of such droplets.

It is apparent therefore that in the manufacture of lubricating greases of this type, the presence of the glycerol enables a non-polar oil to wet the soap, with accompanying displacement of most of the glycerol.   In view of the fact that greases contain not more than 10% of glycerol based on the soap, it is apparent that the equilibrium residual values of glycerol obtained above on the thin soap pellets are high owing to enmeshed free glycerol, and that only a very small quantity of glycerol is actually retained by the soap.

The significance of this unusual type of wetting action, accompanied by the displacement of the wetting agent, will be further discussed in a later publication, particularly in relation to the recrystallization of sodium soaps from a mineral oil medium.

Experimental

Contact Angles. The plate method was used. The soap surface rested on a support that could be accurately levelled, and a small drop of oil was placed on the soap surface. A beam of light from an arc lamp was converged near the oil drop, and the silhouette caused by drop and soap surface was sharply focused through a second lens on a sheet of paper attached behind a sheet of glass. The enlarged outline was pencilled on the paper and the contact angle was then measured with a protractor. An advancing angle was used in all cases.

Oil Analyses. Table III shows inspection data on the oils used in this work.*

TABLE III

INSPECTION DATA ON OILS

	Oil			
	900 vis. 95 V.I.	900 vis. 40 V.I.	100 vis. 95 V.I.	100 vis. 40 V.I.
Gravity, A.P.I.	28.5	22.6	31.4	25.9
Flash, °F.	510	455	360	320
Visc. S.U.S. at 100° F.	889.8	929.1	102.6	101.3
Visc. S.U.S. at 210° F.	81.0	68.3	39.7	—
Viscosity index	97	34	101	†
Pour, °F.	0	−10	+30	−40
Colour, Robinson	9½	9¼	17½	14½
Neutralization No.	0.04	0.28	0.03	0.12

† *Not obtained; value is about 40.*

Acknowledgment

Reference

1. GALLAY, W. and PUDDINGTON, I. E. Can. J. Research, B, 21 : 211-218. 1943.

* *Inspection data obtained from Imperial Oil Limited.*

THE HYDRATION OF THE ALUMINATES OF CALCIUM

V. THE HYDROTHERMAL DECOMPOSITION PRODUCTS OF TRICALCIUM ALUMINATE AT 350° C.[1]

By Herbert Johnson[2] and Thorbergur Thorvaldson[3]

Abstract

When tricalcium aluminate is treated in saturated steam at 350° C. hydrolysis occurs with the formation of a crystalline product of the composition $4CaO.3Al_2O_3.3H_2O$ and calcium hydroxide. The same products result when a 3 : 1 mixture of calcium hydroxide and hydrated alumina are similarly treated. The calcium hydroxide as well as any hexahydrate of tricalcium aluminate formed at lower temperature may be removed from the hydrothermal product by extraction with a solution of acetic acid buffered with calcium acetate.

The 4 : 3 : 3 calcium hydroaluminate crystallizes in colourless elongated rectangular plates with parallel extinction, positive elongation, and low birefrigence. The average refractive index is close to 1.627 and the density 2.71 (at 20° C.). The crystals are probably orthorhombic.

Appreciable dehydration of the product does not occur on heating below 475° to 500° C. Dehydration between 650° and 750° C. in a stream of dry air appears to produce decomposition with the liberation of free alumina and probable formation of the product $12CaO.7Al_2O_3$.

The factors affecting the yield of the 4 : 3 : 3 calcium hydroaluminate and the mechanism of the hydrothermal reactions of tricalcium aluminate and its hydrates are discussed. Readings of X-ray powder patterns of the 4 : 3 : 3 hydroaluminate and its dehydration products are given.

Introduction

The products of the hydrothermal treatment of the aluminates of calcium at 150° C. have been found to be mainly the hexahydrate of tricalcium aluminate and hydrated alumina. Small amounts of other compounds are apparently formed, especially in the treatment of the 5 : 3 calcium aluminate, as indicated by the formation of some birefringent material, the low water absorption during the treatment, and the presence of an excessive amount of combined alumina in the reaction product (4). A study of the hydrothermal behaviour of tricalcium aluminate and its hydrates at temperatures between 150° and 350° C. (2) led to the discovery of a phase crystallizing in thin, transparent, rectangular, prismatic plates of refractive index 1.627. Calculations based on approximate determinations of free calcium hydroxide and combined water in the reaction mixture indicated that this phase is a calcium hydroaluminate with a lower lime–alumina ratio and a much lower water content than hydrated dicalcium aluminate. The present paper gives the results of a further study of this phase and its formation during the hydrothermal treatment of tricalcium aluminate at about 350° C.

Experimental

Preparation of Tricalcium Aluminate

The anhydrous aluminate was prepared from specially purified lime and alumina in platinum vessels as previously described (4). The analysis of the finished product gave calcium oxide, 62.25%, and alumina, 37.76%, as compared with the theoretical values 62.27 and 37.73%, respectively. All tests for free lime were negative.

Hydrothermal Treatments

The hydrothermal treatments were made in a steel bomb of 150 ml. capacity, of the type described by Morey and Ingerson (3), the covered platinum crucibles containing the aluminate being suspended from the plunger of the bomb. The amount of water placed in the bomb was always large enough to give saturated vapour at 350° C., but in some of the earlier experiments slight loss of water occurred during the treatments so that the final concentration of water vapour may have dropped somewhat below saturation.

TABLE I

SUMMARY OF HYDROTHERMAL TREATMENTS

Experiment and sample	Material*	Temp., °C.	Time of treatment, hr.	% Water absorbed (anhydrous basis)
3-a	Anhydrous C_3A	350	36	18.5
3-b	Anhydrous C_3A			18.6
3-c	Anhydrous C_3A			18.3
4-a	Hexagonal hydrate of C_3A	350	12	17.2
4-b	($3CaO.Al_2O_3.10\frac{1}{2} H_2O$)			17.3
4-c	($3CaO.Al_2O_3.10\frac{1}{2} H_2O$)			16.8
7-a	Anhydrous C_3A	350	12	18.8
7-b	Anhydrous C_3A	350	12	18.7
7-c	Anhydrous C_3A	350	12	18.8
8-a,-b,-c	Anhydrous C_3A	350	24	—
9-a	Anhydrous C_3A	350	24	18.8
11-a	Anhydrous C_3A	350	24	18.1
11-b	Anhydrous C_3A	350	24	18.7
11-c	Anhydrous C_3A	350	24	18.5
12-a	Anhydrous C_3A	325	24	18.6
12-b	Anhydrous C_3A	325	24	18.7
12-c	Anhydrous C_3A	325	24	18.7
12-d	Second treatment of Sample 12-c	325	48	20.7
13-a	Anhydrous C_3A	350	24	18.9
13-b	Anhydrous C_3A	350	24	19.5
13-c	Anhydrous C_3A	350	24	19.5
13-d	Anhydrous C_3A	350	24	19.0
14-a	Anhydrous C_3A	350	24	20.0
14-b	Anhydrous C_3A	350	24	21.1
14-c	Anhydrous C_3A	350	24	18.8
14-d	Second treatment of Sample 14-c	350	48	20.1
17-a	Anhydrous C_3A	150	6	31.6
17-b	Anhydrous C_3A	150	24	39.7
18-a	Anhydrous C_3A	350	24	20.4
18-b	Anhydrous C_3A	350	24	20.2
18-c	Anhydrous C_3A	350	24	18.8
18-d	Anhydrous C_3A	350	24	20.2

* Abbreviation used : C_3A = $3CaO.Al_2O_3$.

After rapid initial heating to nearly the desired temperature, which required approximately 40 min., the bomb was placed in an electric air oven adjusted to a temperature of 350° C. ($\pm$ 10°).   At the end of the treatment the bomb was removed from the oven, allowed to cool in air for half an hour, and then cooled to room temperature by immersion in water.   The treated samples were dried over calcium oxide *in·vacuo* for 24 hr. before weighing.   Table I gives the temperature, time of treatment, and the amount of water absorbed (if determined) of a series of hydrothermal treatments.

The absorption of water (retained over calcium oxide) by anhydrous tricalcium aluminate on hydrothermal treatment at 325° to 350° C. for periods of from 12 to 48 hr. varies only from 18.1 to 21.1%.   Variation in the time of treatment (single exposure) has only a minor effect on the amount of water held.   A second treatment for a period of 24 hr. (Expts. 12-*d* and 14-*d*) results in slightly increased absorption of water.   These samples passed four times through the lower range of temperature within which the hexa-hydrate of tricalcium aluminate is the most stable form.   The water retention by the hexagonal hydrate of tricalcium aluminate on similar treatment in the autoclave is of the same order, but slightly lower.   (Expts. 4-*a*, 4-*b*, and 4-*c*). The absorption of water at 350° C. shows a striking difference from that at 150° C. (Expts. 17-*a* and 17-*b*) where the amount approaches rapidly that of the hexahydrate (2).   The significance of the quantitative results will be discussed later.

Separation of the Products of Hydrothermal Treatment

Microscopic examination of the product of the hydrothermal treatment of tricalcium aluminate or its hexagonal hydrate at 350° C. has shown that it contains hexagonal plates of calcium hydroxide, rectangular plates, probably a hydroaluminate of calcium, together with small quantities of other materials (2).   Separation of the two principal components was first attempted by means of the potentiometric titration of a suspension of the mixture using very dilute hydrochloric acid.   It was thus possible to dissolve and neutralize all the calcium hydroxide present without materially attacking the rectangular plate material, but the process was very tedious.   By adding the hydrothermal product to an excess of dilute hydrochloric acid, stirring for a brief period of time, filtering and washing rapidly, a partial separation was also obtained but the rectangular plates were materially attacked.   Similar results were obtained with concentrated solutions of acetic acid.

This led to a study of the action of buffered solutions of acetic acid on the hydrothermal products.   It was found that at room temperature a $0.5 \ N$ solution of acetic acid, with enough calcium oxide added to reduce the acid concentration by one-third, rapidly dissolves calcium hydroxide, the hexa-hydrate of tricalcium aluminate, and calcium carbonate, but does not materially attack the rectangular plates.

The procedure used for the separation was as follows: The finely ground sample (about 1 gm.) of the autoclaved product was added slowly to about 700 ml. of the vigorously stirred buffered solution of acetic acid ($0.33 \ N$

acetic acid, 0.17 N calcium acetate) and the stirring continued for one-half hour. The undissolved solid was then collected in a filtering crucible, washed several times with distilled water, and dried *in vacuo* over calcium oxide. The samples so prepared were found to be composed almost entirely of thin transparent rectangular plates of low birefringence, showing parallel extinction. Two of the refractive indices were very close to 1.627.

The Yield of Rectangular Plate Crystals

Table II gives the yield of insoluble material obtained from a number of hydrothermal products. The yield varies considerably, but this is probably to be expected, considering the variation in the autoclaved material. Microscopic examination indicated the presence of the hexahydrate of tricalcium aluminate in many of the autoclaved samples and this substance was probably

TABLE II

YIELD OF RECTANGULAR PLATE CRYSTALS

Experiment	Time of hydrothermal treatment of tricalcium aluminate at 350° C., hr.	Weight of sample, gm.		% H_2O in autoclaved sample (anhydrous basis)	Yield, rectangular plates, % of hydrated sample
		Anhydrous	Hydrated		
7-*a*	12	0.8792	1.0452	18.8	46.2
7-*c*	12	0.9763	1.1593	18.8	46.6
8-*c*	24	—	0.7078	—	50.7
13-*a*	24	0.5499	0.6539	18.9	51.3
13-*b*	24	0.5892	0.7042	19.5	48.7
14-*a*	24	0.4906	0.5888	20.0	46.5
14-*b*	24	0.4971	0.6019	21.1	53.0
18-*a*	24	0.9176	1.1052	20.4	43.3
18-*b*	24	0.7510	0.9026	20.2	44.3

present to a slight extent in all the hydrothermal products. Losses due to dissolving of the rectangular plates during the extraction possibly varies with the specific surface of the crystalline material. The complete solubility of the hydrothermal products in 5% hydrochloric acid at 65° C. indicated that there was no appreciable amount of hydrated alumina present (4).

The two most important factors in determining the yield of the rectangular plate material appear to be the temperature of treatment and the rate of the initial heating of the autoclave to this temperature. In some experiments in which the temperature was raised very slowly the absorption of water was greatly increased and the yield of rectangular plates materially reduced. Thus in one experiment of four replicates of anhydrous tricalcium aluminate with a long period of heating to 350° C. (two to three hours), the amounts of water absorbed after a 24 hr. treatment at this temperature were 28.4, 29.1, 28.6, and 28.7%, as compared with an average of 19.1% for the 12 to 36 hr.

treatments of Table I. The yield of residue after extraction of two of these samples was 19.5 and 17.3%, or an average of 18.4% as compared with 47.7% in the case of the samples of Table II.

The effect of raising the temperature of the autoclave very rapidly (in about 12 min.) to 350° C. was also of interest. Here the water absorption after a 24 hr. treatment at this temperature was normal (18.1, 18.9, and 19.1%) but the yield of residue after the usual extraction with buffered acetic acid solution was very erratic (35.4%, 2.9%). Microscopic examination of some of these samples showed that the autoclaved material was birefringent and that some crystals of calcium hydroxide were present, but no rectangular plates could be observed. It seems probable that the hydroaluminate was in such a fine state of subdivision that the solubility in acetic acid was abnormally high.

Some determinations of free calcium hydroxide in the hydrothermal products were made using the anhydrous alcohol–glycerol extraction method, but as usual, where dealing with hydrated samples, the results were not entirely satisfactory (2). The maximum value found (in Sample 13-*c*) was 36.8% calcium hydroxide. In this experiment the solid residue after the extraction of the lime by the alcohol–glycerol mixture was filtered off, washed with alcohol, and examined under the microscope. It was composed mainly of the rectangular plates of refractive index 1.627 but showed some isotropic crystals of the hexahydrate of tricalcium aluminate and calcite, the last apparently formed during the protracted determination of the free lime.

The observation was made that addition of calcium acetate to the anhydrous alcohol–glycerol solution speeds up the initial rate of extraction of free calcium hydroxide and reduces considerably the time required for the titration of free lime.

The Ratio of Lime to Alumina in the Rectangular Plates

Quantitative determinations of calcium oxide and aluminum oxide were made on a number of the insoluble residues obtained by extraction of the hydrothermal products with the buffered acetic acid solution. Three preliminary analyses in duplicate gave an average value for the molar ratio of lime to alumina of 1.32. The results of the final series of analyses in which ignited samples were used are given in Table III.

TABLE III

RATIO OF LIME TO ALUMINA IN THE RECTANGULAR PLATES

Sample	Temperature of ignition, ° C.	% CaO	% Al₂O₃	Molar ratio CaO : Al₂O₃
8-*a*	1100	42.2	58.2	1.320
8-*c*	550	41.6	56.8	1.331
9-*a*	1100	42.5	57.7	1.339
14-*a*	1100	42.3	57.6	1.335
14-*c*	1100	42.4	57.7	1.336
				Av. 1.332

The results in Table III indicate definitely that the rectangular plate material has a molar lime–alumina ratio of 4 : 3. Other confirmatory evidence was obtained showing that the ratio is not affected by the method of preparation or extraction. A 3 : 1 molar mixture of calcium oxide and hydrated alumina, which had been treated in the bomb at 350° C. for three days, was found to contain mainly the rectangular plates, together with calcium hydroxide, nearly all the hydrated alumina having entered into combination. After extraction with 50% acetic acid at room temperature, the residue appeared to be composed almost entirely of the rectangular plate material. Analysis of the ignited residue gave 42% CaO and 58% Al_2O_3, a lime–alumina molar ratio of 1.32 : 1. Thus under the conditions in the bomb the same product is formed whether one starts with tricalcium aluminate or an equivalent mixture of lime and hydrated alumina.

The Water Content of the Hydrated 4 : 3 Calcium Aluminate

A number of samples of the rectangular plate material that had been dried to constant weight over calcium oxide were ignited to constant weight. Ignition at 1100° C. in the muffle was necessary for complete dehydration,

TABLE IV

WATER CONTENT OF THE HYDRATED 4 : 3 ALUMINATE

Sample	Weight of hydrated sample, gm.	Temperature of dehydration, ° C.	% Loss (anhydrous basis)	Molar ratio H_2O $\overline{4CaO.3Al_2O_3}$
11-*a*	0.1879	650*	10.73	3.16
11-*b*	0.1805	650*	10.80	3.18
13-*a*	0.2201	1100†	10.76	3.17
13-*b*	0.2206	1100†	10.85	3.20
14-*a*	0.2389	1100†	10.95	3.25
14-*b*	0.2634	1100†	10.58	3.11
			Av. 10.78	3.17

* Heated to constant weight in a vertical tube furnace in a current of purified air dried by magnesium perchlorate.
† Heated to constant weight in electric muffle.

although heating at 650° C. in a current of air dried with anhydrous magnesium perchlorate was equally effective. Nine preliminary ignitions gave an average of 10.8% loss (anhydrous basis). Table IV gives the results of the final series of dehydrations.

The analytical results for the rectangular plate material thus indicate that it is a well defined substance of the composition $4CaO.3Al_2O_3.3H_2O$. There appears to be always present a slight excess of moisture (10.8% vs. 10.2%), but this is probably held by adsorption by the thin platy crystals. This excess moisture is not completely removed by heating until a temperature of 450° C. is reached. The density, determined with a bottle pycnometer using xylol, was found to be 2.71 at 20° C.

Optical Properties of the 4 : 3 : 3 Calcium Hydroaluminate

As stated above, the product is distinctly anisotropic but two refractive indices have a value close to 1.627. Prof. F. H. Edmunds of the Department of Geology has kindly examined some of the samples and reports as follows: "Habit—platy, slightly elongated rectangular grains. Optical Properties— Colorless, anisotropic with low birefringence (0.001 ±). Straight extinction. Slow vibration parallel to length, i.e., positive elongation. Microscopic examination of the material indicated the crystals are orthorhombic."

Thermal Decomposition of the 4 : 3 : 3 Hydroaluminate

The hydroaluminate was dehydrated in an electrically heated vertical tube (Vitreosil) furnace in a current of purified air, thoroughly dried by passing through a long tube packed with anhydrous magnesium perchlorate. The temperature was measured by means of a calibrated iron–constantan thermocouple at the lower, and by a platinum–platinrhodium thermocouple at the higher temperatures, with the thermocouple placed close to the platinum crucible containing the hydrate. Under these conditions the hydroaluminate lost on prolonged heating below 450° C. only the water held in excess of three moles. Heating at 475° C. then produced no change in weight. At 500° C. loss of weight again began but after seven three-hour periods at this temperature the total loss was equal to only about one-half of the water of hydration. On prolonged heating at 650° C. in the current of extremely dry air all the water was eliminated, but, when the hydroaluminate was exposed to the atmosphere in a muffle, heating at 1100° C. was required to effect complete dehydration.

The 4 : 3 : 3 hydroaluminate dried over calcium oxide and the same product after ignition at 1100° C. both dissolved completely in 5% hydrochloric acid at 65° C. Samples dehydrated at 850° to 950° C. (retaining about 0.5% water) also gave clear solutions under the same conditions. Products dehydrated between 650° and 750° C. in the tube furnace produced opalescent solutions in hydrochloric acid. The small residue obtained on filtering this solution was mainly alumina.

X-ray Powder Patterns

Table V gives the data obtained from X-ray powder patterns of (i) the 4 : 3 : 3 hydroaluminate dried over calcium oxide, (ii) the same after dehydration at 650° C., and (iii) after ignition at 1100° C. The hydroaluminate (Pattern 1) and its dehydration product at 650° C. (Pattern 2) give many strong lines in common, although some of the strong lines of the first pattern have no counterpart in the second. Pattern 2 shows no similarity to the patterns given by the "5 : 3" or monocalcium aluminate, whereas Pattern 3 (the hydroaluminate ignited at 1100° C.) is essentially a composite of the lines of the patterns of these two aluminates, indicating that the structure of the 4 : 3 calcium aluminate has been completely destroyed with the formation of the other two aluminates.

TABLE V

READINGS OF X-RAY POWDER PHOTOGRAPHS OF THE 4 : 3 : 3 CALCIUM HYDRO-
ALUMINATE AND ITS THERMAL DEHYDRATION PRODUCTS

No. 1 Dried over CaO at room temp.		No. 2 Dehydrated at 650° C.		No. 3 Ignited at 1100° C.	
Planar spacing, Å	Estimated relative intensity*	Planar spacing, Å	Estimated relative intensity*	Planar spacing, Å	Estimated relative intensity*
3.58	ss	3.57	ss	4.83	ss
3.26	ss	2.79	ss	3.73	ww
3.02	s	2.54	s	3.16	w
2.80	ss	2.36	ss	2.95	ss
2.60	s	2.08	ss	2.65	ss
2.53	s	1.97	w	2.50	s
2.39	ww	1.87	ww	2.42	ss
2.28	s	1.79	w	2.32	ww
2.23	s	1.72	ww	2.18	ss
2.09	ss	1.600	w	2.12	ww
1.96	wu	1.555	ss	1.926	ss
1.90	ww	1.505	s	1.833	ww
1.600	w	1.468	w	1.722	ww
1.570	s	1.427	w	1.684	ww
1.511	w	1.355	s	1.656	s
1.467	w	1.325	w	1.599	s
1.416	ww	1.194	ww	1.519	w
1.164	ww	1.155	w	1.451	ww
1.092	ww	1.117	ww	1.390	w
		1.083	ww	1.335	ww
				1.308	ww
				1.260	ww
				1.175	ww
				1.108	ww

* *ss, very strong; s, strong; w, weak; ww, very weak.*

Discussion and Conclusions

The main reaction that takes place when tricalcium aluminate is treated hydrothermally in the autoclave at 350° C. is apparently the following:

$$3 (3CaO.Al_2O_3) + 8H_2O \longrightarrow 4CaO.3Al_2O_3.3H_2O + 5Ca(OH)_2.$$

Formation of the hexahydrate of tricalcium aluminate occurs as a minor reaction, probably mainly while the autoclave is being heated and cooled.

The main reaction calls for the absorption of 17.8% of water (18.2% on the basis of the experimental 3.17 in place of exactly 3 moles of water) as compared to 18.3%, the minimum experimental value (Table I) and 19.1%, the average for the whole series of single 12, 24, and 36 hr. treatments. Formation of the hexahydrate of tricalcium aluminate (40% H_2O) increases the water requirement greatly. The reaction as formulated above therefore appears, on the basis of water absorption, to take place almost quantitatively when the autoclave is heated rapidly to 350° C. with formation of only minor quantities of the hexahydrate. The average experimental yield (Table II) of

the 4 : 3 : 3 product of 48% (which was almost certainly lowered considerably by partial solution during the extraction of calcium hydroxide, etc.) as against a maximum calculated value of 61% also supports this conclusion. The products formed when the highly hydrated hexagonal form of hydrated tricalcium aluminate is treated in the autoclave at 350° C. are the same. The complete solution of the hydrothermal products in 5% hydrochloric acid at 65° C. indicates that no appreciable quantity of free hydrated alumina is present in the hydrothermal product.

The fact that a 3 : 1 molar mixture of calcium oxide and hydrated alumina, after a similar three-day treatment in the autoclave, gave on extraction with acetic acid a sample of nearly pure 4 : 3 : 3 hydroaluminate, indicates not only that this compound is stable at 350° C., but also that the reaction between hydrated lime and alumina to give the 4 : 3 : 3 hydroaluminate runs to completion under these conditions. This suggests that the mechanism of the reaction between anhydrous tricalcium aluminate and water may involve complete hydrolysis followed by recombination to form the 4 : 3 : 3 compound. This is perhaps further supported by the fact that the highly hydrated hexagonal hydrate of tricalcium aluminate, which hydrolyses more readily than the hexahydrate on solution in water, appears to react quantitatively and rapidly in the autoclave at 350° C. to give the 4 : 3 : 3 hydroaluminate, whereas this is not the case with the more stable hexahydrate under the same conditions.

The relation between the hexahydrate of tricalcium aluminate and the 4 : 3 : 3 hydroaluminate is not clear. The former substance is apparently partially decomposed into calcium hydroxide and the 4 : 3 : 3 hydroaluminate at least when the liquid and solid phases are in contact in the autoclave at high temperatures (2). When the temperature of the autoclave containing anhydrous tricalcium aluminate is raised slowly to 350° C. with the resulting formation of considerable quantities of the hexahydrate during the heating period, the yield of the 4 : 3 : 3 calcium hydroaluminate is low even with prolonged treatment at the maximum temperature. The reactions that occur on hydrolysis of the hexahydrate of tricalcium aluminate in the autoclave appear to be more complicated than the direct formation of the 4 : 3 : 3 product and calcium hydroxide. Considering the experimental work described in the last three papers of this series, as well as the results of other unpublished work, it would appear that this is in better agreement with the assumption of the intermediate formation of a hydrated monocalcium aluminate (6) (perhaps a tetrahydrate at the lower and a dihydrate at the higher temperatures). Preliminary experiments on the hydration of the lower aluminates of calcium in the autoclave also support this possibility.

The behaviour of the 4 : 3 : 3 hydroaluminate on dehydration and ignition is of special interest. The water of hydration is held very firmly, not being liberated freely on heating in very dry air below 475° to 500° C. At temperatures above 650° C. some decomposition with the liberation of alumina apparently occurs. This behaviour may be analogous to the well established

thermal decomposition of the hexahydrate of tricalcium aluminate to give free lime and the 12 : 7 (or 5 : 3) calcium aluminate (5). In the case of the 4 : 3 : 3 hydroaluminate the products should be free alumina and the same aluminate. Whereas the former decomposition can be quantitatively studied by means of the anhydrous alcohol–glycerol method for the direct determinations of free lime, no suitable analogous method for the quantitative determination of free alumina is available. A method based on the solubility of the aluminate and the insolubility of alumina in dilute hydrochloric acid (4) probably does not apply because the alumina formed on the decomposition of the 4 : 3 aluminate at 650° to 750° C. remains so highly dispersed as to possess abnormal solubility in acid. In any case the amount of insoluble alumina obtained on treating the dehydration product, obtained at these temperatures, with 5% hydrochloric acid at 65° C. is very small and does not correspond to the suggested stoichiometric decomposition of the 4 : 3 aluminate.

Although the dehydration products at 650° to 750° C. were not completely soluble, the products obtained at 850°, 950°, and 1100° C. gave clear solutions in 5% hydrochloric acid at 65° C. The X-ray powder pattern of the 1100° C. product indicated a mixture of the 12 : 7 (or 5 : 3) and monocalcium aluminate. No X-ray patterns of the 850° and 950° C. products were made. Thus ignition at 1100° C. (and probably at 850° to 1100° C.) causes recombination of the alumina to form the aluminates which are stable at the liquidus.

· There still remains the possibility that anhydrous 4 : 3 calcium aluminate may have a range of stability at low temperatures. There is no conclusive evidence on this point. The X-ray powder pattern of the product obtained by careful dehydration of the 4 : 3 : 3 hydroaluminate at 650° C. shows many of the strongest lines of the pattern for the hydroaluminate, without any shift, although a number of the strong lines of this pattern are absent. No evidence was found of the strong lines of pentacalcium trialuminate, monocalcium aluminate, or alumina in the X-ray pattern of this dehydration product.

One reference was found in the literature to a 4 : 3 : 3 calcium hydroaluminate. Friedel (1) reports the production of crystals of this composition on heating a mixture of lime and aluminium chloride with water at 500° C. in a sealed tube. No refractive indices were reported. The crystal forms described by Friedel were not observed in any of the writers' samples, but this may have been due to differences in the conditions under which the crystallization took place.

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